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U.S. PATENT APPLICATION

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Invention: FUEL OIL ADDITIVE AND FUEL OIL PRODUCT COMPRISING THE FUEL OIL ADDITIVE

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SPECIFICATION

FUEL OIL ADDITIVE AND FUEL OIL PRODUCTS CONTAINING THE FUEL OIL ADDITVE

Field of the Invention

The present invention relates to an improvement of fuel oil performance, and particularly to a fuel oil additive capable of effectively improving the combustion performance of fuel oils in a combustion chamber of automobile and an oil burning boiler and having energy-saving, decontamination and antifriction effects, and the present invention also relates to fuel oil products added to this kind of additive. This invention particularly relates to a gasoline antiknock additive and a gasoline product containing the antiknock additive.

Background of the Invention

The combustion performance in a combustion chamber of automobile and an oil burning boiler is one of important performance indexes, and it determines whether a fuel oil has properties of energy-saving, environment protection, and the like. For a gasoline product, an important performance index is the antiknock property, and its antiknock index is generally expressed as the average value of an octane number determined by research method (RON) and an octane number determined by motor method (MON). In order to produce a high-octane number gasoline, one method is the improvement of petroleum refining technology by means of catalytic cracking, alkylation, platinum reforming, or the like, but the technological improvement is limited by a variety of factors, including reform and renovation of equipments, funds, a complete set of techniques, and so on; and another method is the addition of a suitable antiknock agent into gasoline.

The energy saving and the reduction of pollution of automobile tail gas exhausted to the environment have become worldwide problems, and they can be realized by three operations:

improvement of the refining technology of petroleum, improvement of engine or combustion equipments (e. g., oil burning boiler) and addition of a suitable additive. Components of energy-saving and decontaminating additives for diesel oil, kerosene, heavy oil, resid are roughly divided into two kinds: one kind is peroxides and another kind is oil-soluble substances containing heavy metals. It has been found in uses that the former is unfavorable to the storage of oils, and the latter results in abrasion of engine and causes new environmental pollution.

Antifriction and anticorrosion effects on engine at work given by adding a mixture (not a synthetic) of a tricarboxylic amide or tetracarboxylic amide and an alkali metal or alkali-earth metal salt into a fuel oil have been disclosed in USP 4,871,375. However, the content of nitrides in the exhaust gas of automobile is increased by the use of amine compounds because of the addition of nitrogen atom. Moreover, effects of this additive on increasing the antiknock property of gasoline, saving energy of oils such as gasoline, diesel oil, kerosene, resid, and the like and reducing the contamination of exhaust gas have not been described in the literature.

A diesel oil additive has been disclosed in USP 5,593,464, and it is a synthetic product of a distilled resid and an alkali metal, alkali-earth metal or rare-earth metal and can inhibit carbon deposit and smoke dust, but whether the additive has an energy-saving effect and an antifriction effect on engine and also whether the additive is applicable to fuel oils other then diesel oil have not been described.

Gasoline additives are roughly divided into two kinds. One kind is pure organic compounds, such as alcohols, aldehydes, ketones, esters and nitrogen-containing compounds. A compound currently widely used is methyl t-butyl ether (MTBE), and ethyl alcohol, methyl alcohol, benzene, t-butyl-toluene, methyl acetate, acetone, isopentane, and the like have also been disclosed in CN 95-111841, 96-102483, 97-108562 and 94-112533. Moreover, halogenated or aminofulvalenes have been disclosed as gasoline antiknock agent in USP 4,264,336 and 5,118,325; alkoxybenzaldehydes and alkoxybenzoates have also been proposed as gasoline antiknock agent in USP 4,444,567; nitrogen-containing compounds such as triazophenols and enamines have been proposed as gaso-line antiknock agent in USP 4,280,458 and 4,417,904. Problems common to these antiknock agents are low effectiveness, large amount, and diseconomy

and inconvenience. The other kind of gaso-line antiknock agent is oranometallic compounds, and they have high effectiveness and small amount. Tetraethyl lead used for many years has been prohibited because of the toxicity of lead. Ferrocene (dicyclopentadienyl iron) and cyclopentadienylmanganese tricarbonyl (wrong word "tricarboxyl" in the original specification, translator) have been proposed as antiknock agent in USP 4,139,349; methylcyclopentadienylmanganese tricarbonyl (wrong word "tricarboxyl" in the original specification, translator) have been proposed as antiknock agent in USP 4,437,436 and is produced in Ethyl Co., USA now; and complexes of cerium and ∀, ∃-diones have been proposed as antiknock agent in USP 4,211,535. Among these compounds, ferrocene has been prohibited because of a harmful effect on engine, the manganese-base antiknock agents have been limited and prohibited because of its poisonous effect on human nerves and environment, and complexes of cerium and ∀, ∃-diones have a too high cost to popularize.

Outline of the Invention

An object of the present invention consists in providing a novel fuel oil additive having effects on improving the quality of oils, lowering the oil consumption, decreasing carbon deposit and redu-cing harmful substances in tail gas of automobile and smoke dust of oil burning boiler as well as reducing abrasion and corrosion of parts of engine.

The present invention also provides novel fuel oils added to the above additive.

Another object of the present invention consists in providing a gasoline antiknock agent and a gasoline added to the additive.

The fuel oil additive provided by the present invention comprises an oil-soluble metal salt of organic acid having the general formula MR, where R is an organic acid radical and the corres-ponding organic acid is a C_1- C_{40} saturated or unsaturated fatty acid, a C_4- C_{40} naphthenic acid, an aromatic acid or alkylphenol, M is a metal cation or a metal complex ion and an clathrate ion, and the corresponding metal is an alkali metal, alkali-earth metal, rare-earth metal, transition metal or main group metal selected from metal aluminum, gallium, germanium, indium, tin or antimony.

The fuel oil additive provided by the present invention includes a gasoline additive, a diesel oil

additive, kerosene additive, heavy oil additive and resid additive. Different from same kind of addi-tives used in existing technique, the present invention selects a suitable metal salt of organic acid as additive or active ingredient of additive, combines good cleaning property, energy-saving property and antifriction property together and has good oil solubility, small amount and high effectiveness.

The present invention especially provides a use of the additive as gasoline antiknock additive. It combines good antiknock property, cleaning property, energy-saving property and antifriction property together and can greatly enhance the gasoline octane number. As shown by service

effects, the additive can be taken as a new-generation product for replacing tetraethyl lead because of its excellent antiknock property.

The metal salts of organic acids used by the present invention can be commercially purchased or synthesized by well-known methods.

The present invention also provides fuel oils added to the additive, including gasoline, diesel oil, kerosene, heavy oil (including resid), the amount is 0.1 – 15 g of the metal salt of organic acid per liter of fuel oil, as compared to common fuel oils, the fuel oils of present invention have better combustion performance, markedly improve the oil quality, are favorable to maintaining normal working conditions of an engine combustion system, and reduce the oil consumption and discharge of pollutants.

Detailed Description of the Invention

As described above, the present invention provides a fuel oil additive which comprises an oil-soluble metal salt of organic acid having the general formula MR, where R is an organic acid radical and the corresponding organic acid is a C_1- C_{40} saturated or unsaturated fatty acid, a C_4- C_{40} naphthenic acid, a C_6- C_{40} aromatic acid or alkylphenol, M is a metal cation, metal complex ion or clathrate ion, and the corresponding metal is an alkali metal, alkali-earth metal, rare-earth metal, transition metal or main group metal selected from metal aluminum, gallium, germanium, indium, tin or antimony.

The fuel oils described by the present invention include such oils as gasoline, diesel oil,

kerosene, heavy oil, resid, and the like.

The present invention especially provides a use of the additive as gasoline antiknock agent.

According to a preferred design of the present invention, the organic acid radical in the metal salt of organic acid originates from a C_1- C_{25} saturated or unsaturated fatty acid, a C_4 - C_{25} naph-phenic acid, aromatic acid or alkylphenol, especially C_{10} or lower the compounds. A metal salt of monocarboxylic acid is preferably used. The gasoline additive with the C_1- C_{25}, preferably C_4 - C_{25} and more preferably $C_1 - C_{10}$ organic acid radical can impart an excellent antiknock property to gasoline.

As saturated fatty acids (organic carboxylic acids expressed by a molecular formula $C_nH_{2n+1}COOH$) and polybasic carboxylic acids described by the present invention, e. g, formic acid, acetic acid, trimethylacetic acid, propionic acid, isopropionic acid, butyric acid, isobutyric acid, valeric acid, isovaleric acid, pivalic acid, 2-ethylbutyric acid, caproic acid, 2-ethylcaproic acid, enanthic acid, caprylic acid, isocaprylic acid, pelargonic acid, capric acid, undecanoic acid, lauric acid, cardanoic acid, hexadecanoic acid, octadecanoic acid, eicosanoic acid, docosanoic acid, pentacosanoic acid, pentatriaconoic acid, hydroxyacetic acid, hydroxypropionic acid, hydroxybutyric acid, hydroxy-succinic acid, tartaric acid (2,3-dihydroxysuccinic acid), citric acid, oxalic acid, malonic acid, suc-cinic acid (butendioic acid), glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, and the like as well as the above acids with substituents; as unsaturated fatty acids (organic carboxylic acids expressed by a molecular formula $C_nH_{2n-1}COOH$) and polybasic carboxylic acids, for example, acrylic acid, methacrylic acid, cis-, trans-crotonic acids, propiolic acid, tetrolic acid, undecenoic acid, octadecenoic acid, oleic acid (cis-9-octadecenoic acid), elaidic acid (trans-9-octadecenoic acid), 9-dodecenoic acid, 9-tetradecenoic acid, trans-9-hexadecenoic acid, cis-6-octadecenoic acid, eicosenoic acid, 2,4-hexadienoic acid, linoleic acid, linolenic acid, eleostearic acid, castoric acid, and the like.

The naphthenic acids described by the present invention include organic acids having a cycloalkyl group in the molecular structure and a carbon number in the above range, for example, monocar-boxylic acid or dicarboxylic acid with a $C_3 - C_{10}$ cycloalkyl, e. g., cyclohexanecarboxylic acid, cyclopentanecarboxylic acid, cyclopentanedicarboxylic acid, cyclopropanecarboxylic acid, cyclo-butanecarboxylic acid, cycloheptanecarboxylic acid,

cyclooctanecarboxylic acid, these carboxylic acids may be formic acid, acetic acid, propionic acid, and the like, e. g., cyclohexylformic acid, cyclohexylacetic acid, cyclopentyldiformic acid, cyclopentylformic-acetic acid, and the like.

The aromatic acids or alkylphenols include benzoic acid, benzene acetic acid, m-, p- and o-phthalic acids, hydroxybenzoic acid, hydrocarbyl-substituted benzoic acid and benzene acetic acid, and the like, aminobenzoic acid, p-hydroxybenzylacrylic acid, abietic acid ($C_{19}H_{29}COOH$), cou-maric acid, phenol, o-methylphenol, 2,4,6-trimethylphenol, 2,3-dimethylhydroquinone, 3-ethyl-catechol, and the like.

The organic acids described by the present invention also include their various isomers.

The effects of the fuel oil additive of the present invention on enhancing the octane number of gasoline, improving the state of combustion of fuel oils and reducing the abrasion of related parts of engine are due to the fact that the oil-soluble metal salt of organic acid described above is used and is characteristic of catalysis, cracking, dilution, excitation and hybridization, therefore, it can effectively enhance the octane number of gasoline, improve the friction of engine, reduce the working resistance of engine and also fully burn the fuel oil, finally achieve effects on enhancing the antiknock property, accelerating the start of automobile, lowering the oil consumption, decreasing carbon deposit, discharging a clean tail gas and extending the service life of an engine system. For the same reason, the metal salt of organic acid used by the present invention similarly achieves effects on cleaning automobile fuel oils such as diesel oil, kerosene, and the like, energy saving and reducing the abrasion of engine as well as effects on cleaning boiler fuel oils such as diesel oil, kerosene, and the like.

On the other hand, the present invention selects suitable metal cations in which the alkali metal may be lithium, sodium, potassium, rubidium or cesium, and the corresponding cation is a monovalent ion, preferably lithium, sodium, potassium ion. The alkali-earth metal is beryl-lium, magnesium, calcium, strontium or barium, and the corresponding cation is a divalent ion, preferably beryllium, magnesium, calcium, barium ion. The rear-earth metal is scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, promethium, samarium, europium, gado-linium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium or the like, preferably scandium, yttrium, lanthanum, cerium, neodymium, and the corresponding cation is a

trivalent or tetravalent ion, preferably a trivalent ion. The transition metal is titanium, zirconium, hafnium, niobium, tantalum, molybdenum, tungsten, ruthenium, osmium, cobalt, rhodium, iridium, nickel, palladium, platinum, silver, gold, zinc, or the like, the corresponding cation is a monovalent, diva-lent, trivalent or tetravalent ion, preferably divalent, trivalent ion, more preferably titanium, cobalt, nickel, zinc. The metal is aluminum, gallium, germanium, indium, tin or antimony, preferably aluminum, tin, and the corresponding cation is a trivalent, tetravalent or pentavalent ion, more preferably a trivalent or tetravalent ion.

A direct reaction method or a metathesis reaction method is commonly used for a method of preparing the metal salts of organic acids.

The fuel additive according to the present invention may comprise one or more of the oil-soluble metal salts of organic acids. Namely, a single metal salt compound of organic acid may be used or two or more oil-soluble metal salts of organic acids may be mixed to become the fuel additive of

present invention, and the ratio of the two or more metal salts of organic acids is not specially restricted so long as they are suitable for a fuel oil used.

The fuel additive according to the present invention may comprise an organic solvent such as alcohol, ether, ketone, phenol, hydrocarbon, ester or nitrogen-containing solvents, or the like, preferably alcohol, ether, phenol, ester, hydrocarbon solvent and nitrogen-containing compound, more preferably alcohol, ether, phenol, hydrocarbon solvent, and their blend will give better effects. The additive can be used more conveniently by reducing its viscosity or dissolution rate with fuel oils. The organic solvent may be blended with one or more metal salts of organic acids.

The organic solvents suitable for the present invention include methyl alcohol, ethyl alcohol, propyl alcohol, isopropyl alcohol, butyl alcohol, isobutyl alcohol, t-butyl alcohol, octyl alcohol, isooctyl alcohol, 2-ethylhexanol, propyl ether, butyl ether, o-, m-, p-methylphenol, dimethylphenol, di-t-butyl-p-cresol, naphthylamine, diphenylamine, triethylamine, p-methylaniline, #120 solvent oil, #200 solvent oil, kerosene, glycol monomethyl ether, diglycol monomethyl ether- ethyl ether-butyl ether, triglycol monomethyl ether-ethyl ether-butyl ether, dibutyl ketone, ethyl acetate, glycol (mono)butyl ether, isoamyl acetate, isobutyl acetate, dibutyl

propionate, dihexyl propionate, diethyl malonate, methyl o-phthalate, ethyl o-phthalate, propyl o-phthalate, octane, and the like.

In the additive according to the present invention, the amount of organic solvent is not specially restricted, and it is preferably 0 – 90 g per 100 g of organic solvent used.

In a preferable embodiment according to the present invention, the fuel oil additive includes gasoline additive, diesel oil additive, heavy oil additive and resid additive. The metal salt of organic acid is preferably selected from compounds synthesized by fatty acids, more preferably saturated fatty acids, an organic acid radical of naphthalenic acid and an alkali metal cation or an alkali-earth metal cation, more preferably an alkali metal salt, an alkali-earth metal salt of a C_1 – C_{10} saturated fatty acid or an alkali metal salt, an alkali-earth metal salt of a naphthalenic acid. Examples of the metal salts of organic acids may be salts of metal ions such as lithium, sodium, potassium, rubidium or cesium, beryllium, magnesium, calcium, strontium, barium, scandium, yttrium, lanthanum, cerium, neodymium, titanium, cobalt, nickel, zinc, or the like and the following organic acids: formic acid, acetic acid, trimethylacetic acid, propionic acid, butyric acid, isobutyric acid, 2-ethylbutyric acid, valeric acid, isovaleric acid, pivalic acid, trimethylacetic acid, caproic acid, 2-ethylcaproic acid, enanthic acid, caprylic acid, isocaprylic acid, pelargonic acid, capric acid, undecanoic acid, lauric acid, tetradecanoic acid, hexadecanoic acid, octadecanoic acid, eicosanoic acid, pentacosanoic acid, pentatriaconoic acid, hydroxyacetic acid, hydroxypro-pionic acid, hydroxybutyric acid, hydroxysuccinic acid, 2,3-dihydroxysuccinic acid, 2-hydroxy-malonic acid, oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, dodecandioic acid, tridecandioic acid, acrylic acid, crotonic acid, maleic acid, fumaric acid, methacrylic acid, propiolic acid, tetrolic acid, undecenoic acid, oleic acid, elaidic acid, octadecenoic acid, eicosenoic acid, 2,4-hexadienoic acid, linoleic acid, linolenic acid, oleostearic acid, castoric acid, cyclohexyl(pentyl, butyl)diformic-(acetic, propionic) acid, cyclopentyl(hexyl, butyl)diformic(acetic, propionic) acid, methylcyclohexylformic-acetic acid, ethylcyclopentylacetic-formic acid, benzoic acid, benzene acetic acid, m-, p- and o-phthalic acids, hydroxybenzoic acid, aminobenzoic acid, abietic acid, metaphthalic acid, p-hydroxybenzylacrylic acid, o-hydroxybenzoic acid, phenol, o-methylphenol, 2,4,6-trimethyl-phenol, 2,3-dimethylhydroquinone, 3-ethylcatechol, or the like.

Any combinations between metal ions and organic acid radicals listed above become organic salts of organic acids suitable for the present invention, e. g., lithium butyrate, sodium butyrate, potas-sium butyrate-caprylate, barium butyrate, zinc butyrate, tin butyrate, lithium valerate, magnesium pivalate, isocaprylates (e. g., zinc 2-ethylhexanoate, lithium 2-ethylcaproate, magnesium 2-ethyl-caproate), lithium trimethylacetate, barium succinate, neodymium acrylate, titanium cyclohexyl-formate, tin o-hydroxybenzoate, magnesium hexadecanoate, lithium undecenoate, cerium cyclo-heptylacetate, sodium pelargonate, calcium acrylate, titanium cyclopentylformate, cerium oleate, nickel cyclopentylformate, potassium eicosanoate, potassium oleate, magnesium laurate, cobalt abietate, and the like.

When the additive according to the present invention comprises one or more of the metal salts of organic acids, the occurrence ratio can be determined according to actual situation, however, a preferable design consists in that the occupying ratio of one of salts is 40 – 80%, and the determination of this salt depends upon metal ions used, the selection is made in order of alkali metals, alkali-earth metals, rare-earth metals, transition metals and other main group metals; when the metals used belong to same group, the ratio of organic acid salt of a metal with the smallest atomic number is preferably 40 – 80%.

According to a preferable design of the present invention, the fuel oil additive is a gasoline antiknock additive. 0.1 – 15 g of the additive (calculated as contained metal salt of organic acid) per liter of gasoline will markedly increase the octane number of gasoline and enhance the anti-knock property of gasoline. Metal salts of $C_1 - C_{10}$ organic acids are preferably used, and their examples are as given above.

The organic acids described by the present invention may also be dicarboxylic acids, tricarboxylic acids or polycarboxylic acid, e. g., substituted o-phthalic acid, dimeric acid, trimeric acid, and the like.

The metal cation described by the present invention may also be an oil-soluble metal complex ion or clathrate ion formed from the above alkali metal ion, alkali-earth metal ion, rear-earth metal ion, transition metal ion or ion of metal aluminum, gallium, germanium, indium, tin or antimony, and the function of ligand in the complex and a receptor in the clathrate compound corresponds to that of an organic acid.

The present inventionalso provides oils added to the described fuel oil additive, including gasoline, diesel oil, kerosene, heavy oil and resid, and the amount is 0.1 – 15 g (as metal salt of organic acid) per liter of fuel oil. Particularly, the oil is a diesel oil having good antiknock property and good cleaning property.

By a large quantity of applications and checks of authorized departments, it has been proved that the fuel oil additive, particularly the gasoline antiknock agent of the present invention com-bines very good cleaning, energy saving, anticorrosion, antifriction functions and effects as well as antiknock property, therefore the additive of present invention can also taken as additive for cleaning, energy saving, anticorrosion, antifriction of gasoline. Namely, the present invention also provides the additive for the purposes of oil cleaning, energy saving, anticorrosion, antifriction.

By a large quantity of applications and checks of authorized departments, it has been similarly proved that the fuel oil additive of the present invention can also be used in diesel and kerosene automobiles and achieve very remarkable functions and effects on cleaning, energy saving, antifriction of related parts of engine and anticorrosion of related parts of engine. Namely, the present invention also provides the additive for the purposes of cleaning, energy saving, anticorro-sion, antifriction additive of automobile fuel oils, such as diesel oil, kerosene, and the like.

By a large quantity of applications and checks of authorized departments, it has also been proved that the fuel oil additive of the present invention can be used in heavy oil, resid and diesel oil and kerosene combustion furnaces and achieve very remarkable functions and effects on cleaning, energy saving, anticorrosion, therefore, the present invention also provides the additive for the purposes of cleaning, energy saving, of fuel oils, such as heavy oil, and the like.

In short, the oil-soluble metal salts of organic acids used by the present invention have no harmful substances, no peculiar smell and no toxicity, do not pollute the environment and harm the health, do not exert adverse effects on parts of engine, greatly enhance the combustion performance of fuel oils with only a very small amount, especially increase the octane number gasoline and impart good antiknock property to gasoline, thus they have advantages of use convenience, high efficiency, low cost and simple production technique; the gasoline added to the

antiknock agent reaches or exceeds the national and international standards in all technical, economic and environmental indexes and do not affect the tail-gas purifier of automobiles, thus they can completely become a new-generation product for replacing tetraethyl lead.

Embodiments and Profitable Effects

The embodiment and profitable effects of the present invention will be explained by the following embodiments and experimental data, but the embodiment range of the present invention should not be limited thereby. Data results from Embodiment 1 to Embodiment 6 among them were measured by Fushun Petrochemical Research Institute, the China Petroleum & Natural Gas Group Co. An equipment used for measurements was an STM-CFR octane number tester made in USA.

Embodiment 1 **Gasoline antiknock additive**

Potassium oleate [$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOK$] 70 g

Methl ethyl ketone (C_4H_8O) 20 g

Ethyl acetate ($C_4H_8O_2$) 10 g

The above three compounds were uniformly mixed and added into gasoline, and an increase of the octane number is shown in Table 1.

Table 1

Addition ratio (G/V) / Index	0	0.1%	0.3%	0.5%	1%
Octane number (RON/MON)	89.3/76.9	90.8/79.6	93.3/83.7	95.4/86.6	98.9/89.3
Antiknock index (RON + MON/2)	83.1	85.2	88.5	91.0	94.1

Embodiment 2

Magnesium laurate [$(CH_3(CH_2)_{10}COO)_2Mg$] 90 g

Glycol monobutyl ether ($C_6H_{14}O_2$) 10 g

Ethyl acetate ($C_4H_8O_2$) 10 g

The above two compounds were added into gasoline, and an increase of the octane number is shown in Table 2.

Table 2

Gasoline	Octane Number of Gasoline (RON)			Octane Number of Gasoline (MON)
	1	2	3	
Gasoline (additive-free)	68.2	83.1	90.7	78.5
Gasoline (containing the additive)				
0.1 g/L	71.0	84.9	92.1	81.5
0.3 g/L	77.2	89.7	94.8	85.6
0.5 g/L	81.6	93.9	96.3	89.7
1 g/L	93.6	96.7	99.9	95.8

Embodiment 3

Cerium naphthenate [(Ce(III)R, R is a naphthenic acid radical] 85 g

Diethyl malonate ($C_7H_{12}O_4$) 5 g

Triethylamine ($C_6H_{15}N$) 5 g

Isopropyl alcohol (C_3H_8O) 5 g

The above four compounds were mixed to prepare an additive and then added into gasoline in the ratio, and an increase of the octane number is shown in Table 3.

Table 3

Addition ratio (G/V) Related index	0	0.1%	0.2%	0.3%	0.5%
Octane number (RON/MON)	90.4/79.8	92.0/83.2	94.2/85.6	96.3/88.9	99.6/92.0
Antiknock index (RON + MON/2)	85.1	87.6	89.9	92.6	95.8

Embodiment 4

Cobalt abietate [(Co(II)R_2, R is an abietic acid radical] ? g (missing)

The above metal salt of organic acid was added into gasoline (in a ratio of 1%), and an increase of the octane number is shown in Table 4.

Table 4

Addition ratio (G/V) Related index	0	0.1%	0.2%	0.3%	1%
Octane number (RON/MON)	93.6/84.0	94.9/85.5	96.2/87.2	97.6/89.2	105.9/92.7
Antiknock index (RON + MON/2)	88.3	90.2	91.7	93.4	99.3

Embodiment 5

Potassium oleate [$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOK$] 50 g

Cobalt abietate [(Co(II)R_2, R is an abietic acid radical] 50 g

The above two metal salts of organic acids were added into gasoline (in a ratio of 1%), and an increase of the octane number is shown in Table 5.

Table 5

Gasoline	Octane Number of Gasoline (Research method)			Octane Number of Gasoline (Motor method)
	1	2	3	
Gasoline free of the agent	55.6	86.3	88.0	82.6
Gasoline containing the agent				
0.1 g/L	62.8	87.1	89.5	84.8
0.3 g/L	70.2	90.8	92.0	88.3
0.5 g/L	78.6	93.5	94.1	90.9
1 g/L	93.9	97.2	109.3	108.9

Embodiment 6

Potassium oleate [$CH_3(CH_2)_7CH=CH(CH_2)_7COOK$] 10 g

Magnesium laurate [$(CH_3(CH_2)_{10}COO)_2Mg$] 10 g

Cerium naphthenate [(Ce(III)R, R is a naphthenic acid radical] 10 g

Cobalt abietate [(Co(II)R_2, R is an abietic acid radical] 10 g

Methyl ethyl ketone (C_4H_8O) 10 g

Ethyl acetate ($C_4H_8O_2$) 10 g

Glycol monobutyl ether ($C_6H_{14}O_2$) 10 g

Triethylamine ($C_6H_{15}N$) 10 g

Isopropyl alcohol (C_3H_8O) 10 g

o-Xylene (C_8H_{10}) 10 g

The above ten compounds were blended into gasoline, and an increase of the octane number is shown in Table 6.

Table 6

Addition ratio (G/V) Related index	0	0.1%	0.3%	0.5%	1%
Octane number (Research method)	91.4	93.1	95.6	97.9	102.3
Antiknock index (Motor method)	85.8	88.1	91.3	94.7	96.9

Embodiment 7

In order to examine the industrialized production of gasoline antiknock additive of the present invention, batch-type production tests of 300 ton gasoline were carried out with a catalytic gasoline as base oil, lithium 2-ethylhexanoate as additive in a #500-16 tank at an addition ratio of 0.22% (g/L) in Fushun First Petroleum Plant, the China Petroleum & Natural Gas Group Co. from September to November, 1997, the gasoline was stored for 3 months and then continuously tested, and data of 5 times tests are shown in Table 7.

Conclusions:

1. After the addition of additive, the gasoline octane number rises by 2.8 unit on the average, the induction period markedly enhances, the antiknock index increases correspondingly, the 50% evaporation temperature slightly falls, and the saturated vapor pressure drops.
2. All the indexes of gasoline after the addition of additive reach or exceed related national standards.
3. The dispersibility of additive in gasoline is good, the addition technique is simple and can be added directly.

Table 7

Item	National Standard	9/30/97	10/5/97	10/12/97	10/19/97	10/26/97	11/2/97
Octane number RON not less than	90	88	90.5	91.0	90.5	89.9	90.5
Octane number MON	/	78.2	79.0	79.8	79.2	78.9	79.5
Antiknock index (RON+MON)/2 not less than	85	83.1	84.8	85.4	85.05	84.4	85.0
Lead content R/L not greater than	0.013	0.0013	/	0.00029	0.00030	0.00022	0.00024
Distillation range							
10% Evaporation temperature not higher than (°C)	70	61.5	51.5	52.0	52.5	56.5	59.5
50% Evaporation temperature not higher than (°C)	120	99.0	93.0	94.0	96.5	94.5	94.5
90% Evaporation temperature not higher than (°C)	190	165.5	163.5	163.5	166.0	164.0	167.0
Distillation end point not higher than (°C)	205	188.5	190.5	192.0	193.0	192.0	193.0
Residual amount % not greater than	2	1.0	1.0	1.0	1.0	1.0	1.0
Saturated vapor pressure KPa not higher than	Winter 88 Summer 74	62	/	42	43	36	34
Actual gum mg/100 mL not greater than	5	1.0	1.8	1.6	2.0	3.0	1.8

Induction period min not less than	480	565	783	720	750	740	660
Sulfur content % not greater than	0.15	0.013	0.018	0.020	0.013	0.017	0.017
Copper sheet corrosion (50 °C, 3 hr) level not lower than	1	1	1	1	1	1	1
Water-soluble acid or alkali	None	None	None	None	None	None	None
Acidity gKOH/100 mL not higher than	3	0.28	0.28	0.11	0.23	0.34	0.31
Mechanical impurities and moisture	None	None	None	None	None	None	None
Doctor test	Pass	Pass	Pass	Pass	Pass	Pass	Pass
Note: 1. The date of adding gasoline into #500-16 tank is September 28. 2. Technological conditions: wax oil 108 t/h, resid 18 t/h, and resid blend ratio 14.3%							

Embodiment 8

To examine the abrasion of gasoline antiknock agent of the present invention on parts of engine, carbon deposit and sediment, the inventors trusted a bench test to Research Institute of Jinzhou Petrochemical Co., the China Petroleum & Natural Gas Group Co. in April, 1998.

A. Equipment

Petter W-1 oil tester imported from the United Kingdom.

B. Sample

Composition of gasoline antiknock agent:

lithium isocaprylate 90 g; ethyl alcohol 2 g; propyl ether 2 g, isoamyl acetate 3 g; diglycol mono-methyl ether 3 g; the five compounds were mixed and then added into gasoline at a prescribed ratio as additive.

Base oil is #90 lead-free gasoline, the above additive was added in a ratio of 0.2% w/w, and a control test without additive was made twice.

C. Test conditions

Severer test conditions for actual use were adopted, and specific data were as follows.

Revolution	1,500 ∀ 10 r/min
Tester reading	70 N
Engine oil pressure	55 x 1,000 Pa
Engine oil temperature	100 ∀ 1°C
Coolant (glycol) temperature	135 ∀ 1°C
Test time	100 hr

1. Abrasion

	(1) Additive is added			(2) No additive is added		
Weight loss of piston ring (mg)	26.2			101.7		
Clearance increment of piston ring opening (concave ring average) (mm)	0.06			0.11		
Side clearance increment of piston ring side (three ring average) (mm)	0.013			0.020		
Weight loss of connecting rod bearing shell (mg)	15.3			15.6		
Cylinder average abrasion (mm)	upper	medium	lower	upper	medium	lower
	0.0025	0.0025	0.00	0.0025	0.015	0.00
Abrasion of valve stem (mm)	0.00			0.00		

2. Sediment of air intake valve

	(1) Additive is added	(2) No additive is added
Weight of sediment (mg)	166.0	255.4

3. Energy saving

(1) Statistic calculation

Average fuel oil consumption for additive-free test is 172.41 sec/100 mL

Average fuel oil consumption for additive-added test is 197.55 sec/100 mL

Oil-saving percentage = [(197.55 – 172.41) ÷ 197.55] x 100% = 12.7%

(2) Weighing

Average fuel oil consumption for additive-free test is 149 kg

Average fuel oil consumption for additive-added test is 132 kg

Oil-saving percentage = [(149 - 132) ÷ 149] x 100% = 10.3%

(3) The oil saving is calculated by switching the additive-added fuel and the additive-free fuel and measuring the oil consumption twice with same engine and under same working conditions (revo-lution and power of engine, engine oil, coolant temperature, engine oil pressure are kept constant). The average value in the whole process of these tests has an oil-saving tendency.

By the control tests of the fuel oil added to the gasoline antiknock agent and the fuel oil free of the gasoline antiknock agent (100 hr each), it can be concluded that

1. The gasoline antiknock agent has an effective and marked antifriction effect from the engine abrasion.

2. The gasoline antiknock agent has a better sediment reducing performance from air valve

sediment.

3. The gasoline antiknock agent has a higher oil-saving performance from different test methods for oil saving.

Embodiment 9

To test the purifying effect of the gasoline antiknock agent of the present invention on automobile tail gas, the inventors trusted it to Liaoning Province Enviromental Monitoring Center in April, 1998.

1. Test contents

The test content is the purifying effect of the gasoline antiknock agent of the present invention on pollutants CO, HC of exhaust gas of automobile, and the antiknock agent is lithium trimethylacetate.

2. Test basis

2.1 GB/T3845-93 "*Measurement of Exhaust Pollutants of Gasoline Automobile, Idling Method*"

2.2 GB14761.5-93 "*Standard for Discharging Idling Pollutants of Gasoline Automobile*"

2.3 IJB3743-84 "*Test Method for Performance of Automobile Engine*"

2.4 "*Bench Control Test Program and Road Surface Test Program of Engine*"

3. Test time

April 10 - 12, 1998

4. Test places

Shengyang City Second Quality Monitoring/Testing Station of Automobile Maintenance, Engine Laboratory and Liaoning Province Environmental Monitoring Center

5. Test conditions

5.1 Instruments and equipments

5.1.1 UREX-201 Automobile tail-gas measurer

5.1.2 D650 Hydraulic dynamometer

5.1.3 CA141 Gasoline engine

5.1.4 QZY-1 Automobile ignition timing tester

5.2 Test oil #90 lead-free gasoline, engine oil, lubricant oil

5.3 Test water temperature 70 - 85°C

5.4 Engine oil pressure 0.2 – 0.5 MPa

6. Test contents and method

6.1 Engine bench test

6.1.1 Bench control test was carried out under equal working conditions.

6.1.2 Start test: automatic start at room temperature 3.2S.

6.1.3 Load characteristic test: The CO and HC concentrations in exhaust pipe were determined under different engine speeds and different loads by changing the load at two speeds of 800 rpm and 1,000 rpm, respectively (A sample head was fixed at the center of exhaust pipe in the depth of 40 cm. The concentrations of CO and HC were read every 5 sec, and 10 readings in total.

6.2 Road surface running test

6.2.1 The model, plate number, engine number and running mileage of a vehicle to be tested were registered first.

6.2.2 An automobile ignition timing tester is installed on an automobile engine, and then the rota-tion speed and ignition advance angle were measured.

6.2.3 Cooling water temperature of engine was measured.

6.2.4. The volumetric concentrations of CO and HC in automobile exhaust pollutants at different rotation speed under idly measured state.

6.2.5 The above gasoline antiknock agent was added into a lead-free gasoline (made by Fushun First Petroleum Plant) in a ratio of 1%, and then it was tested according to the contents of items 6.2.2 – 6.2.4 after running for about 300 km.

6.2.6 During the test period, the fuel oil grade and engine parts of a vehicle to be tested were not replaced, the idling adjustment, fuel/air ratio and ignition timing were kept unchanged, and the cooling water temperature of engine were basically consistent.

7. Test results

7.1 Bench control test of engine

After the gasoline antiknock agent was added, all the CO and HC concentrations reduced under different rotation speeds and load conditions. The CO concentrations reduced by 31.9% on the average and the HC concentrations reduced by 20.1% on the average at a rotation speed of 800 rpm and a load of 5 kg – 20 kg. The CO concentrations reduced by 19.6% on the average and the HC concentrations reduced by 20.1% on the average at a revolution of 1,000 rpm and a load of 5 kg – 20 kg.

7.2 Road surface running control test

After the gasoline antiknock agent was added, all the CO and HC concentrations under different rotation speeds and load conditions reduced. The CO concentrations reduced by 27.0% on the average and the HC concentrations reduced by 23.8% on the average.

7.3 The gasoline antiknock agent of the present invention has a very remarkable effect on reducing the CO and HC concentrations in exhaust pollutants of automobile.

Embodiment 10

To test service performance of the gasoline antiknock agent of the present invention and determine effects of adding the antiknock agent into a gasoline engine on dynamic property and economy, the inventors trusted a bench test to the Shengyang City Second Quality Monitoring/ Testing Station of Automobile Maintenance in April, 1998.

The antiknock agent is lithium pivalate, the test conditions and result are as follows.

1.1 Test place: Shengyang City Second Quality Monitoring/Testing Station of Automobile Maintenance.

1.2 Test time April 11, 1998

1.3 Equipments used: D650 hydraulic dynamometer

SYZZ-1 rotation speed/oil consumption automatic measurer

CA141 gasoline engine

stop watch and control instruments

1.4 Test oil #90 lead-free gasoline, engine oil, lubricant oil

1.5 Room temperature: +18°C, dry-wet difference 85%

1.6 Test water temperature: 65 - 85°C

1.7 Engine oil pressure: 0.2 – 0.5 MPa

2. Test basis

2.1 JB3743-84 "*Engine Bench Control Test Program*"

3. Test contents and methods

3.1 A bench control test was carried out according to requirements identified by both parties under equal working conditions by adopting the original base gasoline and after adding the anti-knock agent.

3.2 Start test: All start-ups are 2.5S under room temperature condition.

3.3 Load characteristic test: The engine speeds drawn up by the "*Program*" are 800 rpm and 1,000 rpm, respectively, and a load characteristic curve of engine is plotted by changing the load at the two speeds.

4. From the load characteristic result, the engine was markedly balanced, the noises were reduced and the oil saving was remarkable after the addition of antiknock agent.

Embodiment 11

To test the oil consumption on road surface running with the gasoline antiknock agent of the present invention, the inventors trusted a control test on energy saving to the Liaoning Province Energy-Saving Monitoring Center in April, 1998.

The composition of gasoline antiknock agent: lithium valerate 80 g; t-butyl alcohol 5 g; glycol

ethyl ether 5 g, octane 5 g; and dibutyl propionate 5 g.

Two automobiles were selected for the test, the one was Liao A77500 Jetta car and the other was Liao A74371 Liberation small truck. The accuracies of all instruments for test were 0.5 – 1.0 grade. A fuel oil used was #90 gasoline produced by the Fushun First Petroleum Plant, and the base gaso-line and a gasoline added to 0.1% (g/L) of the antiknock agent in it were control tested. The test result indicated that the average oil saving percentage was 18.2% for Liao A77500 Jetta car and 16.9% for Liao A74371 Liberation small truck.

Embodiment 12

To test the effect of long-period use of the gasoline antiknock agent of the present invention on automobile, the inventors trusted an uninterrupted application as long as a half year to Head-quarters of Shengyang City Petroleum Co., the China Petroleum & Natural Gas Group Co. The result of application was summaried as follows.

Gasoline antiknock agent formula: lithium isovalerate 95 g, ethyl alcohol 5 g. The amount in gasoline 0.1% (g/L)

Unit: Headquarters of Shengyang City Petroleum Co.

User: Wang Hexin, Executive Deputy General Manager

Use time: October, 1997 – March, 1998

Use model: Buick Century, General Motor Corp., USA

Plate number: Jin A-03197

Comments after use: (1) The dynamic property was improved, the engine had an power increased by one grade and ran more stably, and the general feeling was a markedly improved combustion system and good status of automobile. (2) The oil saving effect was as good as about 15 – 20%. (3) The tail gas discharge was improved (no accurate data because it could not be tested), thus the antiknock agent had a cleaning effect on exhaust pipe. (4) After the antiknock agent was used, no harms to parts were found and no influence were exerted on the tail gas purifier of auto-mobile in a travel of about 10,000 km. (5) From the viewpoint of users, it is hoped that a compre-hensive estimation will be made to advance the additive to the market, facilitate the protection of environmental air and thus bring benefits to mankind.

Embodiment 13

Lithium caprylate was used and added into diesel oil in a weight ratio of 1%, and the result was as follows.

Tested and checked vehicles and models:

1. Liao AX5215, Fukuda diesel car made in Beijing
2. Liao A48982, Isuzu 100P diesel car made in Chongqing
3. Liao A16193, Isuzu diesel car made in Jiangxi

Check-up report

On June 26, 2001, the vehicle to be checked was a Furi diesel truck made in Beijing and running for 20,000 km. 20 L of diesel oil added to the additive in a ratio was filled into an oil tank and no effect was found at the start and, as usual, the exhaust pipe emitted some black smoke because the diesel truck was cold started. After the engine of this truck ran for 10 min, the idling speed of truck felt higher and the noises of engine felt lower than before. After the truck ran for 30 min under the idling state, no temperature rise phenomenon was found by inspecting the water-thermometer, which indicated that the engine temperature was normal. It was found that the tail gas exhausted by engine was much lessened than common diesel oil by inspection. Subsequently, the truck was started, the power ratio of truck clearly felt much higher than before, the start and travel were very stable. After the truck was traveled on the road for 10 min at a uniform speed of 50 km/h, the accelerator pedal felt very light and the dynamic property felt very strong. If the truck was traveled on the road with an extreme speed at this time, it was found that the acceleration of engine was especially quick. When the speed per hour reached 90 km/hr, the noises and tail gas were less than before. After these several items were tested and the truck was put into normal operation, as a result of checking, the oil consumption was reduced by up to 16 – 20% as compared with common diesel oil without adding the additive.

On June 28, 2001, the additive was added in the equal ratio and 20 L of the diesel oil was filled again, the start-up speed of engine clearly rose and the black smoke exhaust by the tail gas also clearly lessened after a cold start, the noises were much lower, but the idling speed of truck was

still higher. The truck was put into normal operation after it ran idly for 20 min. It was found that the oil consumption became much less than last time without any abnormality when the diesel oil was filled again on June 29.

On July 6, 2001, 25 L of the diesel oil was filled in the equal ratio again, the truck was very stable and normal at start and under running condition, and no abnormality of engine was found.

On ? 18, 2001, the engine of this diesel truck was checked, and it was found that the engine oil of engine and the filter core of the oil filter were cleaner than before, and impurities markedly reduced. Moreover, four oil filter tips and surface of piston top were especially clean as if they were just cleaned. In short, after the diesel oil added to the additive was used, the truck was in very good condition from the oil consumption to principal parts of engine. By the checking, it was considered that the additive used had good functions of cleaning, energy saving and the like.

Embodiment 14

Lithium caproate was adopted as additive and was added into #10 diesel oil, the amount was 0.15% (g/L), and the #10 diesel oil being a additive-free base was taken as control.

To test the abrasion of the additive to be tested on parts of diesel engine as well as carbon deposit and sediment, the inventors trusted a bench test to Jinzhou Petrochemical Research Institute, the China Petroleum & Natural Gas Group Co. in 1999. The results are as follows.

1. The diesel oils added to the additive and without the additive were embodied on a diesel engine and ran for a lone time of 100 hr, and it was found that the abrasion of engine using the diesel oil with the additive clearly lessened by measurements and comparison before and after charge.

2. The diesel oil with the additive had a better cleaning effect on sediments of exhaust valve and piston top.

3. Energy-saving effect:

After the additive was added, the energy-saving effect of diesel oil reached 6.8% from the accumulated total oil consumption.

After 1.5 g/L of additive was added, the energy-saving effect could reach 1.19% by contrast to

non-stop switching the fuel oil; and the energy-saving effect could reach 1.5% by addition of 3 g/L as compared with 1.5 g/L of the additive.

4. Conclusions: The additive combines the energy-saving, cleaning and engine abrasion reducing functions and is a good comprehensive additive, and the additive can reduce the number of maintenance and care of engine, extend the service life of engine and has a very striking energy-saving effect.

Embodiment 15

75 g of lithium butyrate, 16 g of lithium oxalate and 9 g of lithium cyclohexylformate were mixed and then the mixture was added into #10 diesel oil in a ratio of 0.1% (g/L), and physical and chemical indexes were tested as follows.

Item		Measuring Unit	Check Result	Check Method
Distillation range	50% Distill-off temperature	°C	270	GB/T6536
	90% Distill-off temperature	°C	325	
	95% Distill-off temperature	°C	335	
Sulfur content		%	0.05	SH/T0253
Sulfur content of thiol		%	0.002	GB/T1792
Acidity		mgKOH/100 mL	0.84	GB/T250
Carbon residue of 10% distillation residue		%	0.28	GB/T268
Ash		%	<0.01	GB/T508
Water-soluble acid or base			none	GB/T259
Cold filtration point		°C	-10	SH/T0240
Cetane number			55	GB/T386
Condensation point		°C	-15	GB/T510
Flash point (closed)		°C	73	GB/T261
Mechanical impurities		%	none	GB/T511
Moisture		%	none	GB/T260
Corrosion (50°C, 3 hr)		Level	1	GB/T5096
Kinetic viscosity (20°C)		mm^3/s	5.441	GB/T265

Embodiment 16

Four compounds, i. e., 40 g of sodium pelargonate, 30 g calcium acrylate, 20 g of titanium cyclooctylformate and 10 g of kerosene were added into #0 diesel oil (called HS-01 fuel oil), and its use conditions and effects for a Liberation 141 model diesel truck are shown in Tables 1 and 2.

Table 1

Item / Fuel	Travel Dir.	Trav. Dist. (km)	Trav. Time (hr)	Fuel Oil Cons. (L)	100km Fuel Oil Cons. (L/ 100)	Load (T)	Start Prop.	Mach. Noises	Dyn. Prop.	Fuel Comb. Prop.	Mach. Oper. Prop.	Tail Gas	C Dep.	Date
	Shengyang-Zhangwu	135	1.7											
#0 Diesel oil	Zhangwu-Shengyang	135	1.7				normal	normal	normal	stable	stable	normal	normal	8/25
	Back-and-forth total[*1]	270	3.4	68.52	5.37	5								
	Shengyang-Zhangwu	135	1.65											
HS-01 Fuel oil	Zhangwu-Shengyang	135	1.65				faster	lower	higher	stable	stable	less	less	8/26
	Back-and-forth total[*1]	270	3.3	61.02	22.59	5								

Weather : 8/25. fine; wind direction: southeast wind, scale 3 – 4; air temperature 17 - 28°C

Weather : 8/26. fine; wind direction: southeast wind, scale 2 - 3; air temperature 20 - 29°C

Table 2

Item / Fuel	Travel Dir.	Trav. Dist. (km)	Trav. Time (hr)	Fuel Oil Cons. (L)	100km Fuel Oil Cons. (L/ 100)	Load (T)	Start Prop.	Mach. Noises	Dyn. Prop.	Fuel Comb. Prop.	Mach. Oper. Prop.	Tail Gas	C Dep.	Date
	Shengyang-Fuxing	244	3.30											
#0 Diesel oil	Fuxing-Shengyang	244	3.30				normal	normal	normal	stable	stable	normal	normal	11/15
	Back-and-forth total[*1]	488	6.60	135	27.66	5								

HS-01 Fuel oil	Shengyang-Fuxing	244	3.30				faster	lower	higher	stable	stable	less	less	11/16
	Fuxing - Shengyang	244	3.30											
	Back-and-forth total*1	488	6.6	61.02	22.16	5								

Weather : 11/15, fine; wind direction: northwest wind, scale 3 – 4; air temperature -9 - 3°C

Weather : 11/16, fine; wind direction: northwest wind, scale 3 - 4; air temperature -11 - 5°C

Embodiment 17

Lithium glutarate was added in a ratio of 0.1% (g/L) and mixed into a #200 heavy oil, and then a control test was carried out with the additive-free heavy oil as control.

Equipment name / Item name		Oil Burning Boiler	Tunnel Kiln	Glass Furnace
Average oil pressure MPa in front of fuel spray nozzle	Control oil	1.20	0.65	0.31
	Test oil	0.70	0.50	0.29
	Change rate%	-41.67	-23.08	-6.50
Thermal efficiency%	Control oil	77.99	10.75	27.51
	Test oil	84.93	11.76	30.37
	Increase	6.94	1.01	2.86
Unit consumption of product heavy oil	Control oil	79.28	600	221.27
	Test oil	72.47	547	200.56
	∀ Change	-6.81	-53	-20.68
Oil saving rate after additive is added		8.59	8.83	9.35